Hard-Soft Acid-Base Catalysts for H_2 Activation

Miles Bartlett, 2026

Climate change caused by the combustion of fossil fuels is a pressing global issue that requires the development of carbon-neutral fuel alternatives. Our aim in the Tate Lab is to develop synthetic liquid fuels used as fossil fuel alternatives in a wide variety of applications. To do so, we aim to cleave hydrogen, which has a high gravimetric (energy by mass) but low volumetric (energy by volume) energy density, in order to hydrogenate carbon compounds such as CO_2. By hydrogenating carbon compounds, we can utilize the highly desirable gravimetric energy density of hydrogen while resolving the storage and transportation issues that exist in its elemental form.

Our method to cleave hydrogen is to develop Hard-Soft Acid-Base (HSAB) catalysts. Hard acids and bases are defined by their low polarizability and preference to ionically bond to each other, while soft acids and bases are defined by their high polarizability and preference to covalently bond to each other. Our catalytic design is based on our consideration of H_2 itself, comprised of the hard acid proton and the soft base hydride, as an HSAB mismatch. Our thesis is that the proton would prefer to bond to a hard base while the hydride would prefer to bond to a soft acid. As such, our catalyst is comprised of a complementary silver-fluoride soft-acid hard-base mismatch so that hydrogen might cleave and form relatively stable but sufficiently reactive hydrogen carriers. These carriers can then be utilized to hydrogenate our carbon compounds and form our liquid fuels.

In order to promote the solubility and stability of our catalyst an ancillary ligand is needed. Due to their favorable steric and electronic effects we have selected N-Heterocyclic Carbenes (NHC) as our ligand of focus. My experimental task was to synthesize the ultra-bulky NHC IPr# used to support our HSAB mismatch. Much of my project was centered around adapting and refining the literature procedure to achieve higher product yield and purity. Common and advanced chemical synthetic methods were used, and Nuclear Magnetic Resonance (NMR) spectroscopy was used to characterize my products. I was able to successfully synthesize IPr#, and future efforts will be focused on improving the yield and purity as well as synthesizing the full catalyst.

An additional aspect of my project was a computational inquiry into the proposed hydrogen activation mechanism via our NHC-supported HSAB catalyst. We are interested in finding out exactly how this reaction happens because approaching our synthesis from a point of greater knowledge will allow us to develop a more targeted approach to catalyst design. Working with Professor Scott, I used Density Functional Theory (DFT) to calculate the energy levels of various transition states to try to find the lowest energy, and thus most favorable, intermediates. As of yet there has been no conclusive evidence supporting a particular mechanism, but the continuation of both my computational and experimental work with should result in significant progress towards the development of our catalyst and the synthetic liquid fuels.

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References

(1) Hopkinson, M.N., Richter, C., Schedler, M. & Glorius F. An overview of N-heterocyclic carbenes. Nature. 2014, 510, 485-496.

(2) Pearson RG. 1963. Hard and Soft Acids and Bases. Journal of the American Chemical Society. 85(22):3533–3539

(3) Qun Zhao, Guangrong Meng, Guangchen Li, Carol Flach, Richard Mendelsohn, Roger Lalancette, Roman Szostak, and Michal Szostak, IPr#—Highly Hindered, Broadly Applicable N-Heterocyclic Carbenes, The Royal Society of Chemistry 2021, 3-4.

(4) Tate, Brandon K., et al. "Heterolysis of Dihydrogen by Silver Alkoxides and Fluorides." *Chemistry–A European Journal* 21.28 (2015): 10160-10169.